AN INVESTIGATION OF SOME SALTS OF l-ABIETIC ACID AND THE DEHYDROGENATION OF l-ABIETIC ACID

A THESIS

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by

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Atlanta, Georgia
1942

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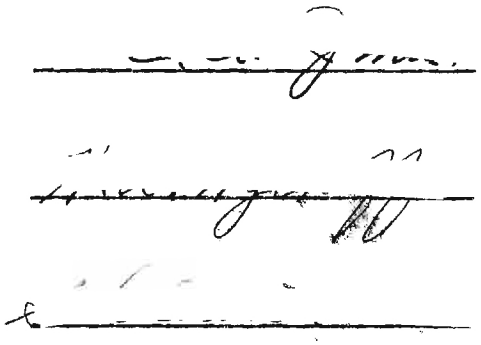

Date Approved by Chairman _____

ACKNOWLEDGMENTS

I wish to express my sincerest gratitude to the State Engineering Experiment Station, at the Georgia School of Technology, and Dr. G. A. Rosselot, its director for sponsoring the project. I should also like to thank Dr. H. M. Waddle for his able dircetion and assistance in overcoming the technical difficulties encountered in the work. In addition to the above mentioned parties I should like to thank Mr. W. W. Gilbert and Mr. Irvin Allen for their valuable assistance in checking certain phases of the work.

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FOREWORD

The work to be described was undertaken for the State Engineering Experiment Station at the Georgia School of Technology, under the supervision of Dr. H. M. Waddle of the Chemistry Department.

The primary and secondary acids obtained from gum or wood rosins are too unstable to permit of any industrial applications as such; however, in the form of mixed esters or as the alkali salts, the rosin acids find some commercial use. The principal acid constituent of rosin is l-abietic acid and it was this acid which was chosen for the investigation. The ultimate object of the work was to convert l-abietic acid to dehydroabietic acid in good yield. The methods to be employed differed from those described in the literature in that a sealed system was used and an attempt was made to direct the course of the reaction by using an hydrogen acceptor.

In the course of the work several methods were developed for the isolation of pure l-abietic acid. The rosin acids in general have the property of forming acid salts of varying compositions with many of the cations and organic bases. The normal salts are known but are usually difficult to prepare. Two salts of l-abietic acid were studied one of which was the well known quarter-sodium salt ($C_{20}H_{29}O_2Na. 3C_{20}H_{30}O_2$) the other was an ammonium salt of indefinite composition.

Pure l-abietic acid can be easily prepared from either of these salts. The acid sodium salt is known to be stable, and the ammonium salt does not undergo any perceptible change on standing. The half-ammonium salt was prepared from pure l-abietic acid, this salt is one which has not been described in the literature.

AN INVESTIGATION OF SOME SALTS OF l-ABIETIC ACID AND THE DEHYDROGENATION OF l-ABIETIC ACID

INTRODUCTION

The oleoresin or gum which is obtained primarily from the pine trees of the southern part of the United States may first be described as consisting of two easily separated mixtures. The basic separation is accomplished by steam distillation, this treatment yields gum rosin and turpentine. After the removal of the oleoresin the pine trunks may either be used for lumber or for the production of wood rosin. The wood rosin is obtained by distillation of the resinous acids directly from the wood leaving wood charcoal in the still. Both gum and wood rosins are refined by furfural treatment and fractional distillation.

The composition of the various rosins, which are classified according to color, varies from some 70 per cent acids in the poorer grades to about 90 per cent in the Commercial Abietic Acid (C.A.A.) manufactured by the Hercules Powder Company. The remainder of the rosin consists of a neutral material termed "resene". The composition of this mixture has as yet not been determined.

A mass of research was undertaken during the early years of the nineteenth century on the composition of the rosin acids. It was soon found that the acid fraction of rosin consists of a highly complex mixture of isomeric and isomorphous acids all

of which have the formula $C_{20}H_{30}O_2$. The voluminous literature which accumulated during the nineteenth century has been complicated by a variety of systems of nomenclature as well as the fact that most of the acids which were reported as pure individual components were in reality mixtures.

In 1912 Kohler (1) drew up a classification scheme of the primary and secondary acids; although several other schemes are to be found in the literature theirs appears to be the most satisfactory in the light of recent developments.

TABLE I

Classification of Resin and Rosin Acids
(Kohler, Duffour, Dupont)*

A. Resin (primary) Acids:

I. Pimaric Acids
(a.) Alpha-Pimaric (dextro)
(b.) Beta-Pimaric (levo)

II. Sapinic Acids
(a.) Alpha-Sapinic (levo)
(b.) Beta-Sapinic (levo)

B. Rosin (secondary) Acids:

I. Levoabietic Acid (Schulz' acid)

II. Intermediate Acids
(a.) Pimarabietic acid
(b.) Sapinabietic acid, etc.

III. Pyroabietic Acids
(a.) Alpha-Pyroabietic acid (dextro)
(b.) Beta-Pyroabietic acid (levo)

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[1]Kohler, J. prakt. Chem., 85, 534 (1912).

*The table includes the modifications of Duffour and Dupont.

More recently the pyroabietic acids have been broken down into mixtures of dehydro, dihydro and tetrahydroabietic acids. The pyroabietic acids had been considered as being advanced stages in the isomerization of l-abietic acid. This was not true, actually dehydrogenation takes place with subsequent disproportionation. Alpha-pyroabietic acid is produced by heat treatment of l-abietic acid in the presence of a palladium catalyst and is now known to contain the dehydro, dihydro, and tetrahydroabietic acids. The beta acid mixture is prepared by heat treatment alone and does not contain the tetrahydro acid.

With the exception of dextro-pimaric acid all the primary and intermediate acids are easily isomerized to l-abietic acid. This isomerization is accomplished with the aid of heat, mineral acids, or ultra-violet light. Of the methods employed the best known is that of Steele (2) who produced isomerization by refluxing the rosin in glacial acetic acid for several hours. The course of isomerization is pictured in Figure I.

The outstanding characteristic of the resin and rosin* acids is their instability even when in a highly purified form.

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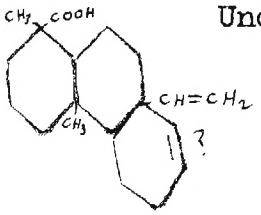
[2]Steele, J. Am. Chem. Soc., 44, 1334 (1922).

*The resin acids are those present in the gum oleoresin after it has been allowed to stand in the air for several days. The rosin acids are produced by the isomerization of the resin acids; this is partially accomplished during the removal of turpentine by steam distillation.

The purest form of l-abietic acid when stored under the most favorable conditions decomposes or rearranges within four to six weeks. This instability is ascribed to the nature of the

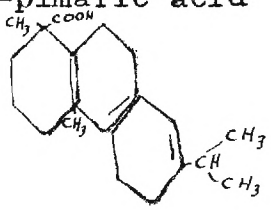
Figure I

The Course of Isomerization of the Resin and Rosin Acids Under the Influence of Mineral Acids



unchanged

d-pimaric acid



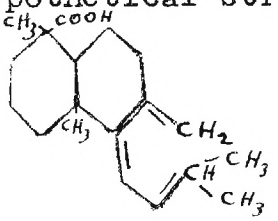
(alpha-pimarabietic acid)

l-pimaric acid

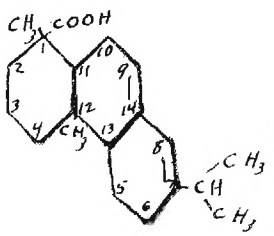
alpha-sapinic acid ⟶ (alpha-sapinabietic acid)

beta-sapinic acid ⟶ (beta-sapinabietic acid)

Hypothetical structure

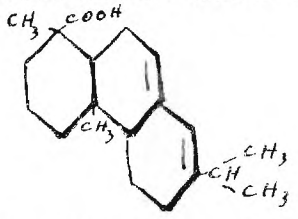


for sapinic acids.

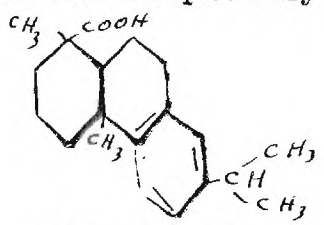


l-abietic acid

molecule itself, as can be seen from the following structures l-abietic acid does not contain an aromatic nucleus whereas dehydroabietic acid does contain one completely aromatic ring.



l-Abietic Acid



Dehydroabietic Acid

Any casual inspection of the literature reveals a very wide variation in the physical properties of the rosin and resin acids. For example the melting point of l-abietic acid is given as 156-60, 172-173, 181-183, and 172-176; the optical rotation varies as given in the literature from minus 68 to minus 105°. The melting point of any sample of acid varies considerably with the rate of rise of the bath temperature, consequently special apparatus is required for the determination of the melting point. At best the melting point is a very poor indication of the purity of a sample as there is undoubtedly further isomerization, shifting of bonds and oxidation of the compound at the melting point. The latest work on l-abietic acid indicates a melting point of 170-173° and rotation of about minus 100° for the purest form (3 and 4). Any individual acid is capable of existing in several different

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[3]Palkin and Harris, J. Am. Chem. Soc., 56, 1936 (1934).

[4]Fieser and Campbell, ibid., 60, 159 (1938).

isomeric forms and any particular method of purification probably results in the more or less complete isolation of one of these forms.

The methods used to isolate pure l-abietic acid may be divided into two distinct types. The earlier work was all carried out by the fractional crystallization of the acid from organic solvents, ethyl alcohol being the most widely used. Depending upon the source of the rosin from six to eleven crystallizations were usually necessary. Any lengthy fractional crystallization of the acids is complicated by the tendency of the acids to undergo rapid atmospheric oxidation. To minimize this effect Dupont and Uzac (5) used small amounts of hydroquinone in the recrystallization vessels.

The other method of purification and the one which has come into most frequent use takes advantage of the property of the acids to form salts with most of the inorganic cations as well as with organic bases. Here too the acids are unusual in that they have a pronounced tendency to form acid salts rather than the normal salts. Of the numerous salts described in the literature only one has been used to any great extent. The quarter-sodium salt ($C_{20}H_{29}O_2Na.\ 3C_{20}H_{30}O_2$) was described by Dupont, Desalbres, and Bernette (6); they prepared the salt from the pure acid but apparantly did not use it as a means

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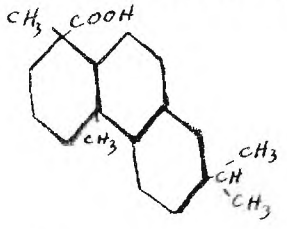
[5]Dupont and Uzac, Bull. soc. chim., 35, 394 (1924).

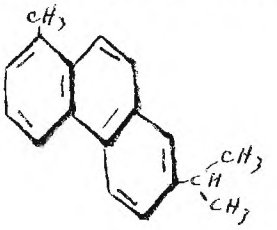
[6]Dupont, Desalbres, and Bernette, Bull. l'inst. pin, No. 22, 349 (1926).

of purifying the acid. At about the same time Palkin and Harris (7) used the quarter-sodium salt to prepare the pure acid by a process of fractional crystallization of the salt.

The problem of stabilizing l-abietic acid involves the dehydrogenation of the molecule to a form containing at least one aromatic ring. This has been accomplished in two ways, the first and earliest work being directed toward the preparation of retene (8) by drastic dehydrogenation accompanied by decarboxylation. Although a stable product is obtained in good yield it is not an acid, thus limiting its usefulness.



S, Se, or Pd catalyst
300-350° C.



l-Abietic Acid

Retene

The more important method of stabilization depends on a milder dehydrogenation of the acid to dehydroabietic acid (9 and 10). This is accomplished with the aid of a palladium or nickel catalyst at temperatures around 200 to 250°C. The reaction is complicated by disproportionation of hydrogen in the reaction mixture as follows:

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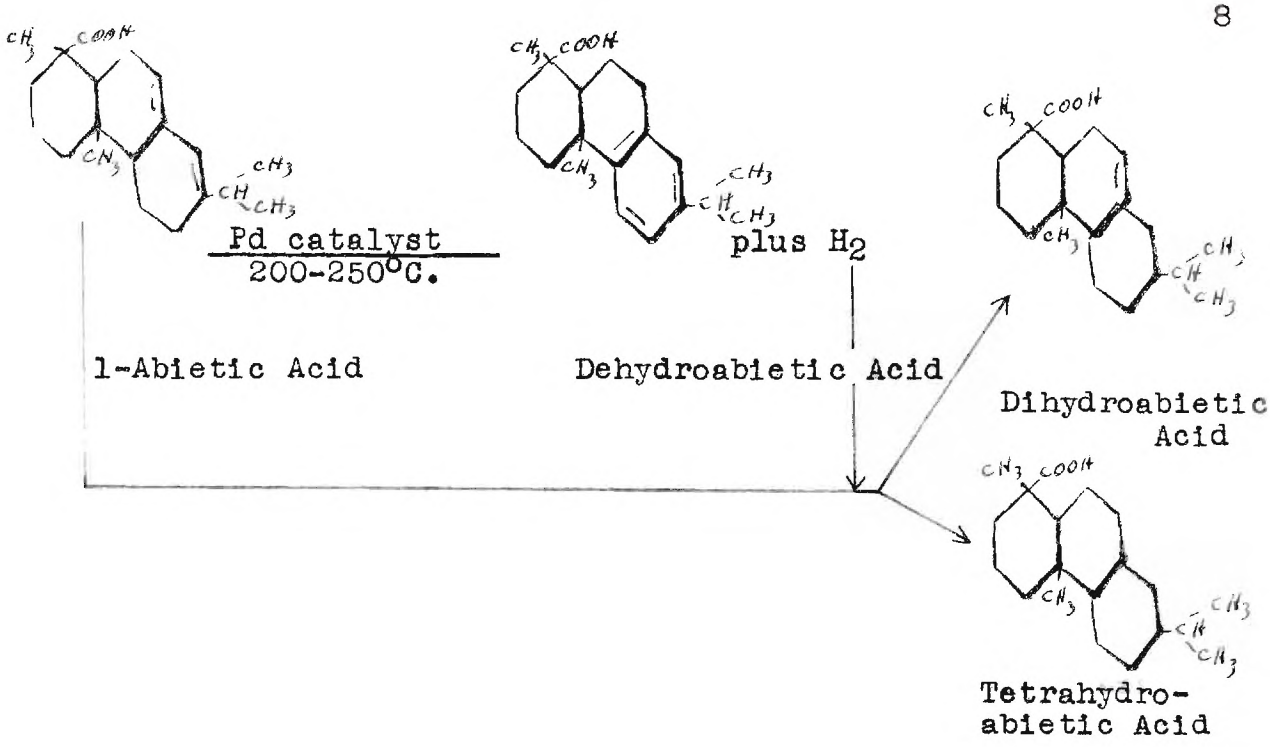
[7]Palkin and Harris, J. Am. Chem. Soc., 56, 1936 (1934).

[8]Diels and Karstens, Ber. 60B, 2323 (1927).

[9]Fleck and Palkin, J. Am. Chem. Soc., 59, 1593 (1937).

[10]Fieser and Campbell, ibid., 60, 159 (1938).



Another method which has been used for the preparation of dehydroabietic acid (11) involves the oxidation of l-abietic acid with SeO_2 to 6-hydroxy abietic acid and subsequent dehydration of the sodium salt with glacial acetic acid. The hydroxy acid is unstable and must be stored as the complex sodium salt. The over all yield reported by Fieser and Campbell (11) was approximately 25 per cent.

A logical method of attack on the problem of obtaining dehydroabietic acid in good yield would be to control the disproportionation of hydrogen by employing an hydrogen acceptor. That is, if the hydrogen can be removed from the acid as it is split off, the reaction could only lead to the

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[11] Fieser and Campbell, J. Am. Chem. Soc., 60, 167 (1938).

formation of dehydroabietic acid. The use of hydrogen acceptors is not new by any means, Adkins, Richards, and Davis (12) having successfully employed both ethylene and thiophene free benzene as hydrogen acceptors. Where the character of the reaction mixture would allow their use, such compounds as 5-pentene (2-amylene), acetone, or the unsaturated fatty acids could conceivably act as hydrogen acceptors. In general it may be said that the ideal hydrogen acceptor should be highly unsaturated, readily available, react irreversibly with hydrogen under the conditions of the reaction, be stable against polymerization, and easily removed from the reaction product.

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[12]Adkins, Richards, and Davis, J. Am. Chem. Soc., 63, 1320 (1941).

PREPARATION OF ABIETIC ACID USING THE QUARTER-SODIUM SALT

Any procedure employed for the preparation of pure l-abietic acid depends for its success upon the complete removal of relatively small amounts of a neutral uncharacterized material termed "resene". According to Kessler, Lowy, and Faragher (13) "resene" acts as an oxidizing agent when in contact with the acid.

The quarter-sodium salt is formed from an alcoholic solution of the rosin containing slightly less than the calculated quantity of 8 N NaOH. Since "resene" is quite soluble in alcohol, it is possible to remove it more or less completely, depending upon the scheme of purification employed and to a marked degree upon the skill of the worker. The procedure employed in this work may be outlined as follows:

1. Formation of the 1/4 sodium salt from Commercial Abietic Acid by addition of the calculated quantity of sodium hydroxide.
2. Filtration of the sodium tetraabietate, washing with aqueous alcohol to remove as much "resene" as possible.
3. Conversion of the 1/4 sodium salt to the acid by addition of a mineral acid, and then reconversion to the salt.

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[13]Kessler, Lowy, and Faragher, J. Am. Chem. Soc., 49, 2998 (1927).

4. Repetition of steps 1, 2, and 3 until an acid is obtained whose melting point and rotation become constant.

EXPERIMENTAL

Nine hundred and ten grams of Commercial Abietic Acid was placed in a three liter round-bottomed flask and dissolved in 900 cc of 85-90 per cent ethyl alcohol by refluxing gently for fifteen minutes. Seventy cubic centimeters of 8 N NaOH diluted with 100 cc of 95 per cent alcohol was added to the hot solution. After the hot solution was filtered through a buchner funnel, it was placed in a large beaker and allowed to stand overnight.

The sodium tetraabietate came out as a thick mass of fine light yellow crystals of the consistency of cottage cheese. The mass was thinned down with several hundred cc of alcohol to aid in the filtration of the slurry. The salt was filtered, washed with 80 per cent alcohol and sucked dry on the funnel. Several grams were removed for the determination of the melting point. Drying of the sample was accomplished with the aid of an Abderhalden apparatus using P_2O_5 in the drying pistol and operating at a temperature of 97°C.

The damp filter cake was placed in a large round-bottomed flask fitted with a reflux condenser and dissolved in 1400 cc of 90 per cent ethyl alcohol by gentle refluxing. Forty-two cubic centimeters of 12 N HCl (based on the quantity of NaOH used to form the salt plus a slight excess) in 50 cc of alcohol

was added to the hot solution. A quantity of NaCl settled out and was filtered off. The hot solution was poured into a large beaker and allowed to stand over night. The acid came down as a mass of very fine light yellow crystals. This material was filtered, washed with aqueous alcohol to remove as much resene as possible and finally with water to remove any NaCl which might have been present . Here again a small sample was taken for the determination of the physical constants.

In the manner described, four complete cycles were carried out; that is, the salt and acid were each prepared four times. The properties which these compounds possessed are given in Table II.

TABLE II

Physical Constants of Compounds Obtained

Compound		m. p.	$(X)_D^{24}$ *
I.	1/4 Na salt	157-163	
II.	1/4 Na salt	168-174	
III.	1/4 Na salt	172-178	
IV.	1/4 Na salt	177-183	
Ia.	Abietic acid	145-150	-85°
IIa.	Abietic acid	158-163	$-89\frac{1}{2}^{\circ}$
IIIa.	Abietic acid	161-165	-95°
IVa.	Abietic acid	160-164	-97°

*The symbol "X" will be used in place of alpha for the specific rotation throughout this thesis.

The constants listed in Table II were determined during the early part of the work and are of no value other than to indicate the course of purification. An acid was obtained possessing essentially constant properties; however, as the melting point determinations were made in an open bath and no stem correction applied they are of little value. Also the samples were immersed at room temperature and no attempt was made to regulate the rate of rise of the bath temperature.

After having communicated with several research laboratories* which have published work of this nature a method of determining melting points was arrived at; the determinations were subsequently carried out as follows:

1. Total immersion Wheeler melting point thermometer (A. H. Thomas Co., Philadelphia, Pennsylvannia) used with the Hershberg (13) form of apparatus.
2. Sample immersed some ten degrees below the expected melting point.
3. Rate of rise of bath temperature between one and two degrees per minute.

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*Private communications from Dr. William P. Campbell, Harvard University, Department of Chemistry, Cambridge, Massachusetts, and Drs. Fleck and Palkin, U. S. Department of Agriculture, Bureau of Agricultural Chemistry and Engineering, Washington, D. C.

[13]Hershberg, Ind. Eng. Chem. Anal. Ed., 8, 312 (1936).

Although the over-all yield of pure l-abietic acid was very small due to the many operations involved, it is of interest to note that the best yield of 1/4 sodium salt is obtained when 0.1875 times the calculated quantity (based upon the previously determined acid number of the rosin) of NaOH required for complete neutralization is used.

PREPARATION OF l-ABIETIC ACID USING THE AMMONIUM SALT OF INDEFINITE COMPOSITION

There have been two ammonium salts of l-abietic acid described in the literature. The first of these was an acid salt prepared by Mach (14) who described it as precipitating in the form of white prismatic crystals. The formula given for the salt was ($C_{19}H_{27}O_2NH_4 \cdot C_{19}H_{28}O_2$); unfortunately no physical constants were listed. The normal salt was reported by Dupont and Desalbres (15) who described it as crystallizing in the form of small prisms having the following physical constants: m. p. 110° and $(X)_J$ -90°.

The work to be described involves the use of an ammonium salt of indefinite composition. From the analysis of the salt it has been impossible to write a reasonable formula. Although this is somewhat unusual it is not unprecedented, as Steele (16) has isolated iron and chromium salts of similar character. Two different methods of preparation and purification of the salt are given. One uses gaseous ammonia and the other, concentrated ammonium hydroxide. In the first case, purification is accomplished by extraction with acetone on a mechanical shaker or by the use of soxhlet extractors. The

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[14]Mach, Monatsh., 15, 627 (1894).

[15]Dupont and Desalbres, Bull. soc. chim., 39, 493 (1926).

[16]Steele, J. Am. Chem. Soc., 44, 1333 (1922).

second method employs various organic solvents to obtain the pure crystalline salt.

EXPERIMENTAL

PREPARATION OF CRUDE AMMONIUM ABIETATE USING GASEOUS AMMONIA

As nothing was found in the literature regarding the preparation and properties of the salt being described, it was necessary to conduct numerous experiments to determine the optimum conditions for preparing the salt. Of the many attempts made, the following experiments are representative of the procedures which gave the best results.

I

Sixty-two grams of Commercial Abietic Acid was powdered and dissolved in 450 cc of acetone at room temperature. Ammonia gas was generated by heating concentrated ammonium hydroxide in an erlenmeyer flask. The gas was passed through a calcium chloride absorption tube, and then into the abietic acid solution. After the gas had been passed into the solution for ten minutes, the warm solution was set aside to cool. The salt came down as a finely divided semi-crystalline white solid which was filtered through a buchner funnel and washed with acetone. The filtrate, after standing overnight, yielded an additional quantity of salt. A yield of 41 grams or 76 per cent, calculated from the acid number of

the Commercial Abietic Acid used, was obtained.

(The acid number may be defined as the number of milligrams of KOH required to neutralize one gram of acid, and is calculated according to the following formula:

$$\text{Acid Number} = \frac{\text{cc NaOH X N. F. X 56.1}}{\text{grams of sample}}$$

$$\text{Per cent Acid} = \frac{\text{acid number}}{185.6}$$

The acid number of the Commercial Abietic Acid used in this work was determined by a procedure outlined by the Hercules Powder Company. A 2.500 gram sample of the acid was dissolved in 20 cc of benzene and 50 cc of neutralized ethyl alcohol containing one cubic centimeter of phenolphthalien was added. Sodium hydroxide was standardized against potassium acid phthalate and the titration made with a wide open buret until the end point was nearly reached. An acid number of 162 was found or 87 per cent acid. Determination of the acid number of purified l-abietic acid in alcohol, using phenolphthalien as indicator gave the theoretical acid number (185.6) within experimental error.)

A small quantity of the ammonium salt was heated gently; whereupon a gas was given off which was basic to litmus. The red viscous liquid which resulted was poured onto a glass dish where it solidified to a brittle semi-transparent solid. This material was powdered and was found to have a melting point of 90-95° (uncorr.). The compound, or more probably, the mixture of compounds, was not characterized.

II

Five hundred grams of Commercial Abietic Acid was powdered and dissolved in 1465 cc of acetone (slight warming was necessary to affect solution). Ammonia was generated, as in Experiment I, and passed into the acetone solution until the odor of ammonia could be detected above the container. The salt had a tendency to form in large clumps around the delivery tube, and it had to be scraped off and broken up frequently. The mixture was set aside over-night to complete precipitation, and an additional 400 cc of acetone was added to prevent excessive clumping of the salt.

After filtering the salt and washing it with acetone, part of it was placed in the thimbles of six large soxhlet extractors, in which acetone was used as the extracting solvent. After four hours of extraction, the defects in the procedure became evident. Continuous extraction with warm acetone dissolved a considerable quantity of the salt, and the dissolved salt had a tendency to clog the system as it cooled in going through the side arms. The remainder of the salt was extracted in the same equipment with ethyl alcohol, but here again the same difficulty was encountered to a more marked degree. Three hundred and sixty grams of dry amorphous salt was obtained.

Several large continuous extractors were designed and built in an attempt to obtain a cold continuous extraction

of the salt. These attempts failed as the salt had a tendency to pack down to a solid mass and would not allow the solvent to flow through. It was finally decided to attempt the purification by means of a mechanical shaker.

III

The following experiment represents a general procedure which was repeated several times with essentially the same results.

Commercial Abietic Acid was dissolved in acetone at room temperature using a ratio of four cubic centimeters of acetone to one gram of acid. The solution contained in a large round-bottomed flask was warmed to 45°C., and a slow stream of ammonia gas (tank of gas obtained from the Ohio Chemical Co.) was bubbled into the warm solution until the odor of ammonia could be detected above the container. On cooling, ammonium abietate precipitated as a yellow amorphous solid. The salt was then filtered through a buchner funnel and washed with cold acetone. It was then placed in a large round-bottomed flask, and the contents covered with acetone and shaken vigorously for several minutes on a mechanical shaker. The acetone layer was decanted, a fresh portion was added, and the shaking continued. This procedure was repeated until the salt was white and the acetone layer was colorless. After it was filtered, the salt was air-dried. The yield was approximately 56 per cent as calculated from the acid number of the C. A. A.

and on the assumption that the salt corresponded to the formula ($C_{20}H_{29}O_2NH_4 \cdot C_{20}H_{30}O_2$). The salt obtained had the following constants: m. p. 149-150° (corr.) (1° rise per minute) and $(X)_D^{30}$ -44.8° (1 per cent solution in dioxan).

PREPARATION OF CRUDE AMMONIUM ABIETATE USING CONCENTRATED AMMONIUM HYDROXIDE

As gaseous ammonia is not as readily available as concentrated ammonium hydroxide, and as the quantity of gas used is very difficult to measure; an investigation into the possibilities of using ammonia solutions was undertaken. After numerous experiments had been performed on the use of aqueous ammonia, a procedure was developed whereby the crude ammonium salt could be prepared rapidly and in excellent yield. Concentrated ammonium hydroxide was used under closely controlled conditions. Failure to follow the exact procedure (given below) resulted in the formation of gelatinous products which could not be purified.

I

A thousand gram sample of Commercial Abietic Acid containing 87 per cent acids was dissolved in 3300 cc of acetone. The solution was heated slowly to 45°C., and 190 cc of 15 N ammonium hydroxide (sp. gr. 0.90) was added slowly with vigorous agitation. The flask containing the solution was stoppered and placed in cold water to allow the ammonium

salt to crystallize. The quantity of ammonium hydroxide used in this experiment was 1.98 times the calculated quantity necessary for the one-half ammonium salt ($C_{20}H_{29}O_2NH_4 \cdot C_{20}H_{30}O_2$). As cooling had been too rapid, the partially precipitated salt was redissolved and the solution allowed to cool slowly to room temperature, whereupon the bulk of the salt precipitated. The mixture was then placed in an electric refrigerator overnight.

The salt was filtered, washed with acetone, and air-dried. An actual yield of 702 grams was obtained. Basing the calculation of the per cent yield on the assumption that the salt is composed primarily of the one-half ammonium compound, a yield of 78.5 per cent was obtained. The assumption that the crude salt is composed chiefly of the acid salt is based on the fact that when the salt is crystallized repeatedly, its properties approach those of the salt prepared from pure l-abietic acid whose composition was determined by analysis. (See page 39.)

II

A sample of 750 grams of Commercial Abietic Acid was dissolved in three liters of acetone and the solution heated to 45°C., then 2.06 times the calculated quantity of 15 N ammonium hydroxide was added. The mixture was allowed to cool slowly to room temperature, whereupon the bulk of the

salt came down. The mixture was then placed in the refrigerator over-night. The salt was filtered off and washed with acetone on the buchner funnel (before filtering an additional liter of acetone was added to aid in filtration). The yield of crude ammonium salt was 637 grams or 94.6 per cent (calculated as in the preceding experiment) of theoretical.

In this experiment, as well as in most of the others, it was found that the salt had a tendency to come out as a gelatinous mass. It was possible to prevent the formation of this material by gently stirring the warm solution obtained immediately after the addition of ammonium hydroxide. When this was done, the salt began to come out in a few minutes as a light yellow somewhat granular material.

III

A sample of 750 grams of Commercial Abietic Acid was dissolved in three liters of acetone, the solution was heated to 45°C., and 132 cc of 15 N ammonium hydroxide was added. The warm solution was stirred gently for several minutes while it cooled to room temperature. The salt soon precipitated as the amorphous solid. After the flask and contents were allowed to remain in the refrigerator over-night, the contents were diluted with a liter of acetone and filtered, then washed with more acetone, and finally dried. The yield of crude salt was 592 grams or 88.2 per cent.

IV

Fifty grams of Commercial Abietic Acid was dissolved in one liter of acetone and the solution heated slowly to 45°C. Six cc of 15 N ammonium hydroxide was added to the warm solution and the flask and contents set aside to cool slowly to room temperature. The salt came out as fine white needles. After filtering, washing with acetone, and drying, 15.6 grams of salt was obtained. After the filtrate was cooled in the refrigerator, an additional 5.4 grams of salt was formed; however, this salt did not appear to be as pure as the first batch. The gross yield was 47 per cent. Thus it was seen that a crystalline salt could be obtained when a large volume of acetone was used. The yield of pure salt was rather low and the use of such large quantities of acetone was prohibitive; therefore, this line of work was not continued.

V

One hundred grams of Commercial Abietic Acid was dissolved in 400 cc of acetone and the solution heated to 45°C. Nine and six tenths cc of 15 N ammonium hydroxide (the calculated quantity necessary for the formation of the one-half ammonium salt) was added slowly while the mixture was stirred gently. After cooling the flask and contents over-night in the refrigerator, the product was filtered, washed with

acetone, and air-dried. A yield of 26 grams or 29 per cent was obtained. It was thus seen that the use of the calculated quantity of ammonium hydroxide resulted in a very poor yield.

PURIFICATION OF CRUDE AMMONIUM ABIETATE USING ORGANIC SOLVENTS AND THE PREPARATION OF l-ABIETIC ACID FROM THE SALT

From a study of the solubility behavior of crude ammonium abietate in various organic solvents several solvents were found which were suitable for preparing the crystalline

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Table III

Solubility* of Crude Ammonium Abietate in Organic Solvents

Solvent	T_1	T_2
Acetone (crude salt)	2 g./liter @ 30°	10g./liter @ 58°
Acetone (cryst. salt)	1.6g./liter @ 30°	10g./liter @ 58°
Alcohol	2.2g./liter @ 30°	40g./liter @ 78°
Benzene (less than	1g./liter @ 28°)	18g./liter @ 80°
Dioxan	10g./liter @ 28°	160g./liter @ 101°

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*These solubilities were determined by the addition of salt in small weighed portions to the solvent until no more would dissolve. In general the values varied considerably depending upon the purity of the salt used.

salt. Aqueous alcohol, aqueous dioxan, and benzene all yielded crystalline products of varying degrees of purity.

EXPERIMENTAL

I

A hundred gram sample of the crude ammonium salt obtained in Experiment I (page 20) was dissolved in two liters of ethyl alcohol (95 per cent) at a temperature of 75 to 80°, and 200 cc of water was added slowly to the warm solution. The resulting solution was allowed to cool to room temperature and then placed in the refrigerator over-night.

The crystalline salt was filtered, washed with alcohol, and dried in a vacuum desiccator. A yield of 42 grams or 42 per cent was obtained of a compound which possessed the following physical constants: m. p. 149° (corr.) (1.2° rise per minute) and $(X)_D^{25}$ -61.5° (1 per cent solution in dioxan).

Twelve grams of the above salt was suspended in 100 cc of 95 per cent ethyl alcohol and 30 cc of 1 N HCl added. At this point it was necessary to heat the mixture to affect solution of the resulting acid. After all the acid had gone into solution, water was added to incipient crystallization. The beaker and contents were placed in the refrigerator to obtain more complete precipitation of the acid.

(The point of incipient crystallization is reached when the acid begins to crystallize from the hot alcohol and water

solution. To obtain more complete precipitation of the acid after the initial crystallization has begun, excess water is added with vigorous stirring, whereupon the bulk of the acid precipitates as very small crystals. In order to obtain a purer product, the solution containing the acid is warmed to 50° and water added with gentle stirring until the first signs of permanent turbidity appear (incipient turbidity). Upon slowly cooling the turbid solution, white triangular plates are formed.)

The l-abietic acid was filtered, washed with a solution of 70 per cent alcohol in water, and dried in a vacuum desiccator. A yield of 8.2 grams or 68 per cent was obtained. This compound possessed the following physical constants: m. p. 166-170° (corr.) (1.4° rise per minute) and $(X)_D^{27}$ -74.5° (1 per cent solution in 95 per cent EtOH). The sample was dissolved in 50 cc of hot alcohol, filtered while hot to remove solid impurities, again heated until clear, and water added until incipient turbidity was obtained. The acid,after cooling over-night, was filtered, washed with 70 per cent alcohol and dried as before. A yield of 6.8 grams or 86 per cent was obtained from a sample weighing 7.9 grams. The product possessed the following physical properties: m. p. 166-70° (corr.) (1.4° rise per minute) and $(X)_D^{27}$ -82°. The sample of acid was crystallized once more, giving a yield of 86 per cent and the following physical properties: m. p. 167-170.5° (corr.) (1.4° rise per minute) and $(X)_D^{27}$ - 89°.

II

A sample of 30.2 grams of crude ammonium abietate prepared with the use of concentrated NH_4OH was dissolved in 750 cc of 95 per cent ethyl alcohol at 75°C., and 150 cc of water was added slowly while stirring the hot solution. Crystalline ammonium abietate was obtained by cooling the solution in the refrigerator over-night. The salt was filtered, washed once with acetone, and allowed to dry in the air; 12.3 grams of fine white needles was obtained. The salt possessed the following physical constants: m. p. 156° (corr.) (1.3° rise per minute) and $(X)_D^{28}$ -59.1° (1 per cent solution in dioxan). The above sample was recrystallized from 95 per cent ethyl alcohol. The resulting needles had the following constants: m. p. 154° (corr.) (1.2° rise per minute) and $(X)_D^{28}$ -67.5°. The results of the analysis* of this salt follow:

Anal. Calculated for $C_{20}H_{29}O_2NH_4.C_{20}H_{30}O_2$: C, 77.23; H, 10.22: N, 2.25; Found: C, 74.70; H, 10.27; N, 3.28.

From this analysis no formula for a definite compound could be written. (see page 15)

A 4.7 gram sample of the recrystallized salt was suspended in 150 cc of 95 per cent EtOH; 17 cc of 1 N HCl was added, and the mixture shaken in a separatory funnel. Solution took

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*The analyses given throughout this work were made by the Huffman Microanalytical Laboratories, 505 Majestic Building, Denver, Colorado.

place in a few seconds (excess of HCl was used). The alcoholic solution was stirred, warmed, and water was added until incipient crystallization took place. The mixture was then placed in the refrigerator to permit more complete precipitation. After filtering, washing with water and drying, a yield of 71 per cent was obtained. The acid was recrystallized from 95 per cent EtOH; the resulting acid possessed the following constants: m. p. 168-171° (corr.) (0.95° rise per minute) and $(X)_D^{28}$ -83.5° (1 per cent solution in 95 per cent EtOH). The following analysis was obtained for the acid:

Anal. Calculated for $C_{20}H_{30}O_2$: C, 79.42; H, 10.00. Found: C, 79.29; H, 9.94.

III

An 80 gram sample of crude ammonium abietate obtained in Experiment II (page 21) was dissolved in 2700 cc of benzene at 75 to 80°C. The solution was allowed to cool to room temperature, whereupon the salt came out as fine white needles. The mixture, after cooling over-night in the refrigerator, was filtered and washed with benzene. It was found that the salt had a tendency to occlude resene and this material could not be washed out. The salt was recrystallized from 2300 cc of benzene, as before, and a white crystalline product obtained in a yield of 35.7 grams, or on a weight basis 35.7 per cent. The salt possessed the following properties: m. p. 145.5° (corr.) (0.9° rise per minute) and $(X)_D^{24}$ -60°.

Twelve grams of this salt was suspended in 100 cc of 95 per cent alcohol and the mixture heated to 45°. Eleven cubic centimeters of 2 N HCl was added and the resulting solution heated to the boiling point. Water was added to incipient turbidity and the solution set aside to crystallize. After the mixture was cooled over-night in the refrigerator, the acid was filtered, washed with 70 per cent alcohol, and dried under vacuum. A yield of 7.6 grams or 63 per cent was obtained of an acid having the following physical constants: m. p. 151-168° (corr.) (2.2° rise per minute) and $(X)_D^{27}$ -84°. This sample on recrystallization possessed the following properties: m. p. 163-164° (corr.) (1.1° rise per minute) and $(X)_D^{27}$ -79°. The use of benzene as a crystallizing medium was abandoned due to the inconsistency found in the physical properties of the acid obtained in this and other experiments.

IV

One hundred grams of crude ammonium abietate obtained in Experiment III (page 22) was dissolved in a liter of dioxan at 95 to 100°C., and one hundred cc of water was added to the hot solution. After the salt had begun to crystallize, the flask and contents were placed in the refrigerator over-night to complete the crystallization. The crystalline salt was filtered, washed with 50 per cent aqueous dioxan, and finally dried in a vacuum desiccator. The yield obtained was 38 grams, or calculating on the weight basis, 38 per cent of salt which

gave the following constants: m. p. 146° (corr.) (1.0° rise per minute) and $(X)_D^{24}$ -60.5° (1 per cent solution in dioxan).

Twelve grams of the crystalline salt was suspended in 100 cc of 95 per cent EtOH, and the mixture heated to 45 to 50°C. Fifteen cubic centimeters of 2 N HCl was added to the warm mixture and the resulting solution heated to the boiling point. Water was added to incipient turbidity, and the beaker and contents were placed in the refrigerator to aid in crystallization. After the acid was filtered, washed with 70 per cent alcohol, and dried under vacuum; it was obtained in a yield of 8.2 grams or 68 per cent. This acid possessed the following properties: m. p. 165-169° (corr.) (1.3° rise per minute) and $(X)_D^{27}$ -79°. A 7.9 gram sample of the acid was recrystallized from aqueous alcohol, as previously described, and 6.9 grams of acid resulted (87.4 per cent) having the following properties: m. p. 165-169° (corr.) (1.3° rise per minute) and $(X)_D^{27}$ -87°. The acid was recrystallized a second time, andwas recovered with a yield of 87.5 per cent, and was found to have the following physical constants: m. p. 167-170° (corr.) (1.2° rise per minute) and $(X)_D^{27}$ -89°.

V

The preceding three experiments involved the use of the ammonium salt which had been crystallized once from various solvents. The following experiments use the salt after crystallizing it twice from the same solvent.

A sample of 29.8 grams of crystalline ammonium abietate obtained in Experiment I (page 25) was dissolved in 700 cc of 95 per cent ethyl alcohol at 75 to 80°, and the hot solution was filtered. The filtrate was warmed again and 70 cc of water added. After crystallization had begun at room temperature, the mixture was placed in the refrigerator over-night to obtain more complete precipitation of the salt. The crystalline salt was filtered and washed with 70 per cent alcohol, after which it was dried in a vacuum desiccator. A yield of 12.3 grams or 41.3 per cent was obtained. The salt possessed the following constants: m. p. 153.5-154° (corr.) (1.2° rise per minute) and $(X)_D^{25}$ -70.5°.

Eleven and one tenth grams of the salt was suspended in 100 cc of 95 per cent alcohol and the mixture heated to 40-45°C. Fifteen cc of 2 N HCl was added and the resulting solution warmed to approximately 70°C. Water was added to the hot solution until incipient crystallization was obtained. After cooling the mixture in the refrigerator over-night, the acid was filtered, washed with 70 per cent alcohol and dried. A yield of 7.49 grams or 67.4 per cent was obtained; this acid possessed the following constants: m. p. 168-172° (corr.) (1.2° rise per minute) and $(X)_D^{27}$ -99°. This acid (7.25 grams) was recrystallized by dissolving in 50 cc of hot 95 per cent alcohol (the solution was filtered at this point to remove insoluble matter) and water added to the hot solution to incipient turbidity. After cooling, filtering, washing with aqueous alcohol

and drying, a yield of 5.15 grams or 71 percent* was obtained. This acid possessed the following constants: m p 168-172° (corr.) (1.2° rise per minute) and $(X)_D^{27}$ -98°. The l-abietic acid was crystallized a second time by dissolving in 35 cc of hot 95 per cent alcohol, and sufficient water was added to the hot solution to obtain incipient crystallization. After filtering, washing, and drying, the acid was obtained in 88 per cent yield. This acid possessed the following constants: m p 167-169.5° (corr.) (1.5° rise per minute) and $(X)_D^{27}$ -99°.

VI

A sample of 17.9 grams of crystalline ammonium abietate obtained in Experiment IV (page 29) was dissolved in 300 cc of dioxan at approximately 95-100°C. The solution was filtered hot and allowed to cool to room temperature, whereupon the salt crystallized. The flask and contents were placed in the refrigerator over-night to aid to crystallization. The salt was filtered, washed with aqueous dioxan, and dried in vacuum. The compound was obtained in 43.8 per cent yield based upon the weight of sample taken. This salt had the

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*The variations in yield obtained in recrystallizing l-abietic acid are due to variations in concentration of the aqueous alcohol used in crystallizing, purity of the acid, and the length of time employed in cooling. By progressive dilution of the filtrates, practically all of the acid can be recovered.

following physical constants: m. p. 148.5-149° (corr.) (1.2° rise per minute) and $(X)_D^{25}$ -69.5°.

Seven and fifteen hundredth grams of the salt was suspended in 100 cc of 95 per cent alcohol and the mixture warmed to 40-45°C. Ten cubic centimeters of 2 N sulfuric acid was added; the mixture was stirred until solution was complete and water was then added to the warm solution to the point of incipient crystallization. The mixture was treated as described in the preceding experiment and 4.7 grams of acid was obtained. This acid possessed the following constants: m. p. 165-169° (corr.) (1.2° rise per minute) and $(X)_D^{27}$ -93°. Four and three tenth grams of the acid was recrystallized from aqueous alcohol, as previously described. A yield of 3.7 grams or 86 per cent was obtained of an acid having the following properties: m. p. 166-171° (corr.) (1.3° rise per minute) and $(X)_D^{27}$ -96°. This acid was recrystallized once more with an 82.3 per cent yield being obtained. The physical constants found were; m. p. 167.5-170.5° (corr.) (1.5° rise per minute) and $(X)_D^{27}$ -98°.

SUMMARY

The best over-all results were obtained by crystallizing the crude ammonium salt twice from dioxan. An acid of essentially constant properties was obtained when the purified salt was converted to the acid andthe acid then

crystallized twice; however, one crystallization after the formation of the acid was sufficient. The principal objection to the use of aqueous dioxan or aqueous alcohol in the crystallization of the crude ammonium abietate is the low yield obtained in the initial crystallization as well as in the second crystallization; also, some difficulty is encountered in the laboratory fractionation of the aqueous filtrates. It was found that more efficient purification was obtained by one recrystallization of the salt than by two recrystallizations of the acid; that is, the physical properties approach a maximum more rapidly.

Figure II

Flow Sheet Showing Purification Scheme
(Using Aq. EtOH)

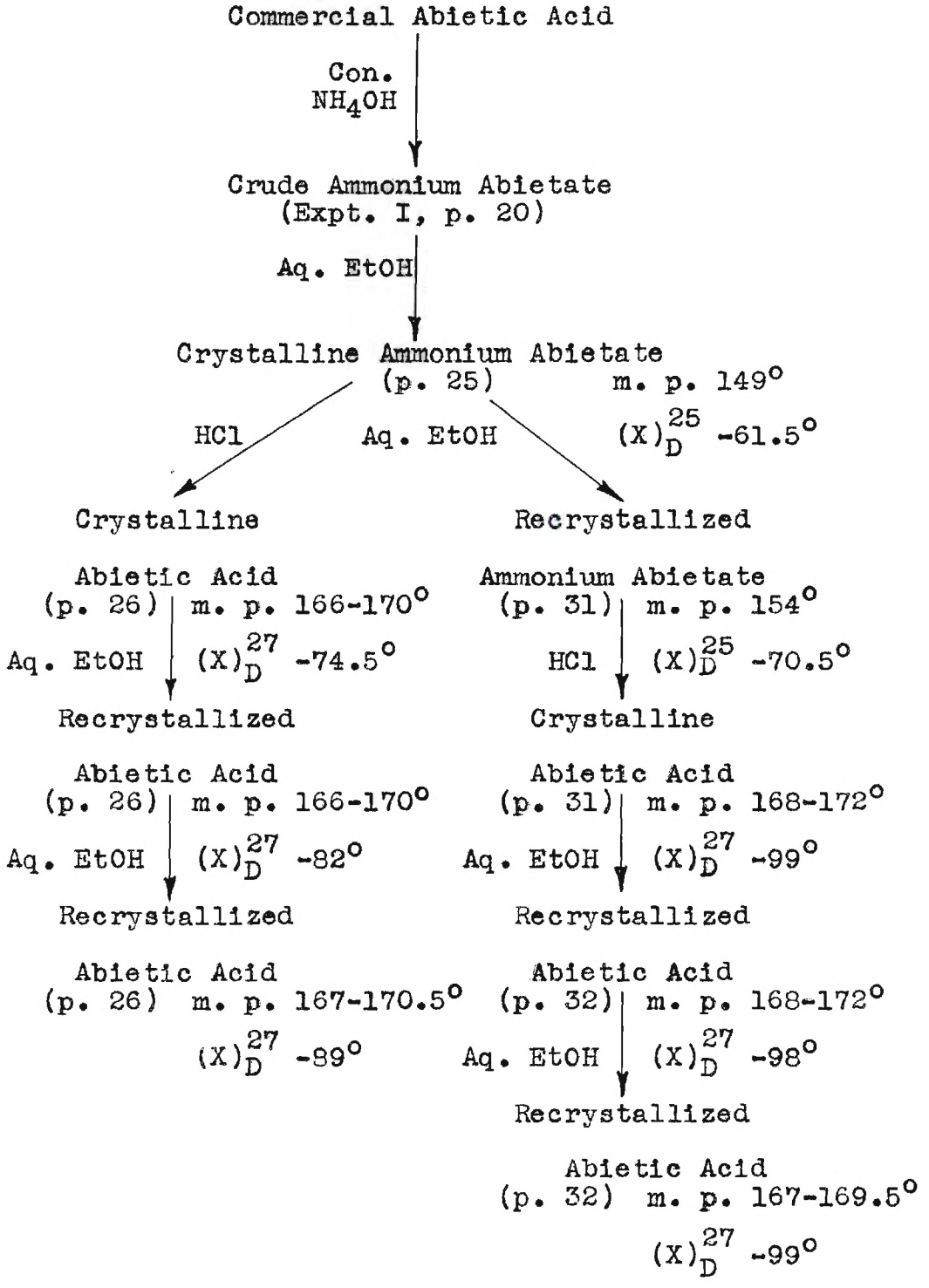
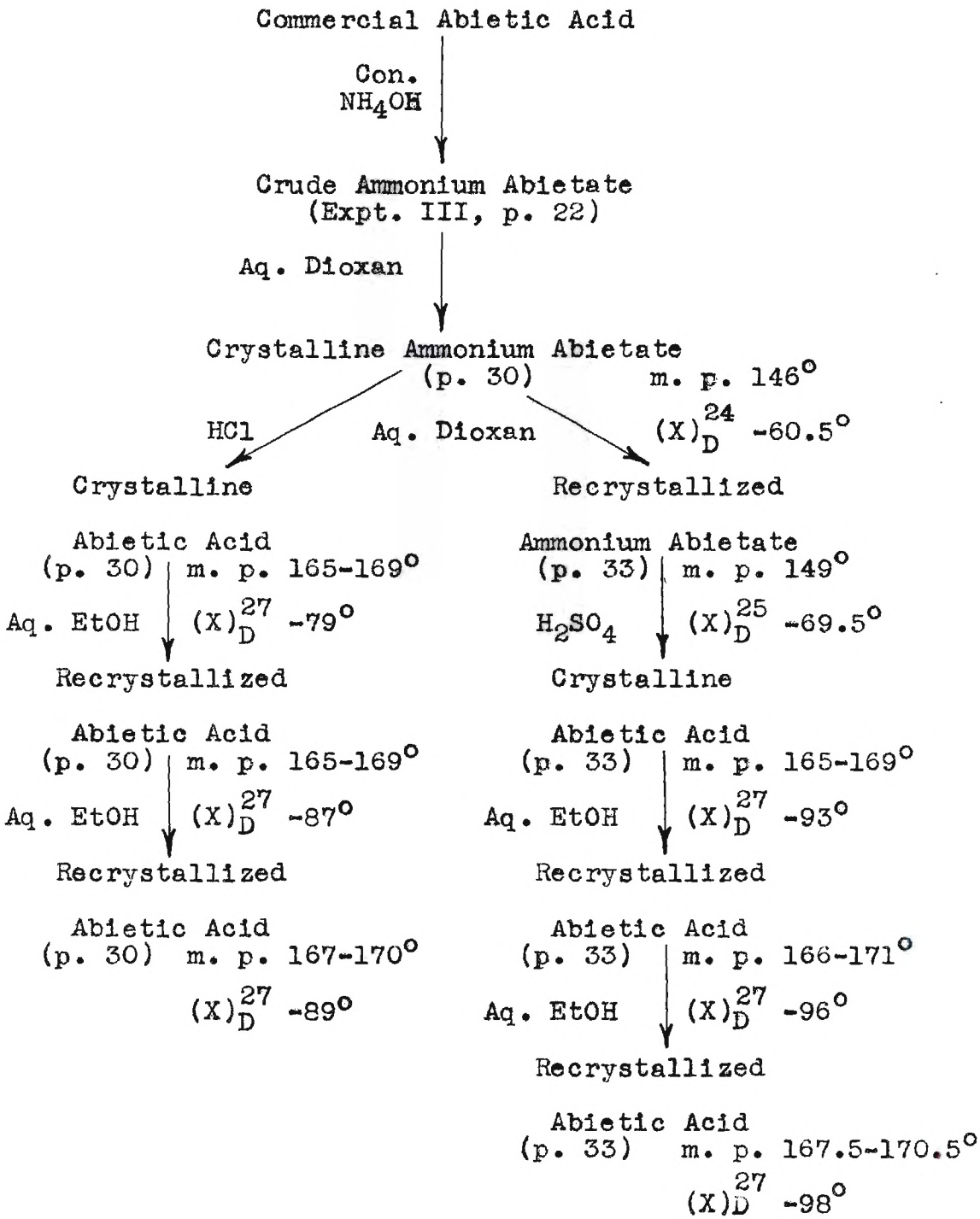


Figure III

Flow Sheet Showing Purification Scheme
(Using Aq. Dioxan)



THE USE OF A MIXTURE OF ACETONE AND DIOXAN IN CRYSTALLIZING AMMONIUM ABIETATE

The following experiment represents the culmination of a series of experiments whose object was to obtain the maximum yield of crystalline salt from the crude.

One hundred grams of crude ammonium abietate obtained in Experiment II (page 21) was dissolved in 800 cc of hot dioxan at a temperature of 95 to 100°C. Five hundred cubic centimeters of acetone was added rapidly to the dioxan solution, after it had been allowed to cool slightly. The bulk of the salt crystallized within a few minutes, and the mixture was then placed in the refrigerator over-night. The crystalline salt was filtered and washed with 400 cc of acetone on a buchner funnel, after which it was spread out on paper towelling and allowed to air-dry. A yield of 59 per cent was obtained on a weight basis (100 grams of crude salt gave 59 grams of crystalline product).

The dried salt was dissolved in 500 cc of boiling dioxan and 350 cc of acetone added rapidly to the hot solution, after which crystallization immediately began. After most of the salt had crystallized, the beaker and its contents were placed in the refrigerator for several hours. The salt was filtered and washed with 300 cc of acetone and allowed to air-dry over-night.

For the third crystallization the dried salt was

dissolved in 500 cc of hot dioxan, and 250 cc of acetone was added rapidly to the slightly cooled solution. Crystallization once again began almost immediately after the addition of acetone. After cooling the mixture over-night, 200 cc of acetone was added to break up the closely packed crystals, and the salt was then filtered. After the compound was washed with an additional 200 cc of acetone, it was placed in a vacuum desiccator to dry. After three crystallizations, a forty gram yield of white needles was obtained. The salt possessed the following constants: m. p. 155° (corr.) (1.3° rise per minute) and $(X)_D^{25}$ -66°.

A portion of the salt (13.8 grams) was suspended in 150 cc of 95 per cent ethyl alcohol and the mixture warmed to 40°C. Twenty cubic centimeters of 2 N HCl was added, whereupon the salt was converted to the alcohol soluble l-abietic acid. The solution was filtered to remove any insoluble matter; then the filtrate was warmed to 45°C., and 25 cc of water was added to produce incipient crystallization. The mixture was placed in the refrigerator over-night, and the precipitated acid was filtered and dried under vacuum. A semi-crystalline acid was obtained which possessed the following properties: m. p. 168-171° (corr.) (1.2° rise per minute) and $(X)_D^{25}$ -94°. This acid was crystallized from aqueous alcohol, and after it was filtered and dried possessed the following constants: m. p. 168.5°-172° (corr.) (1.6° rise per minute) and $(X)_D^{25}$ -98° (1 per cent soln. in 95 per cent EtOH).

PREPARATION OF THE HALF-AMMONIUM SALT OF l-ABIETIC ACID

An ammonium salt whose analysis showed a definite composition corresponding to the formula ($C_{20}H_{29}O_2NH_4 \cdot C_{20}H_{30}O_2$) was prepared from purified samples of l-abietic acid. This salt crystallized in the same form as the salt of indefinite composition, and was prepared with the aid of either gaseous ammonia or concentrated aqueous ammonia.

EXPERIMENTAL

I

Three grams of l-abietic acid(m. p. 165-167°) (corr.) and $(X)_D^{28}$ -85° (1 per cent solution in 95 per cent EtOH) was dissolved in 50 cc of acetone, the temperature of the solution raised to 45°C., and ammonia gas passed into the solution for several minutes. The solution was allowed to stand at room temperature, whereupon fine white needles of ammonium abietate formed. After the salt was washed with acetone and dried under vacuum; it was sent to a commercial laboratory, along with the acid from which it had been prepared, for analysis. The results of the analyses follow:

Anal. Calculated for $C_{20}H_{30}O_2$: C, 79.42; H, 10.00; Acid Number, 185.6. Found: C, 79.11; H, 9.88; Acid Number, 184.1 $\pm$ 1.0

Anal. Calculated for $C_{20}H_{29}O_2NH_4 \cdot C_{20}H_{30}O_2$: C, 77.23; H, 10.22; N, 2.25. Found: C, 77.29; H, 10.21; N, 2.27.

Unfortunately no constants were determined for the above salt, because it was not until later that a solvent was found in which the salt was sufficiently soluble to permit the determination of optical rotation. Also, it was later found that the melting point of the salt varies considerably with the rate of rise in bath temperature. To obtain the physical constants of the acid salt the following two experiments were performed.

II

Three grams of a sample of l-abietic acid, which had the following physical constants: m. p. 166-168° (corr.) (1.3° rise per minute) and $(X)_D^{28}$ -80°, was dissolved in 50 cc of acetone and the temperature raised to 45°C. Ammonia gas was bubbled through the solution from a glass bulb having very small holes punched through it; by this means, no large local concentration of gas was obtained. The solution was agitated while the gas was admitted, and after about a minute the salt began to crystallize. The mixture was allowed to cool over-night; then it was filtered, washed with acetone, and finally recrystallized from hot ethyl alcohol. One gram of fine white needles was obtained (no attempt was made to obtain more of the salt from the mother liquor). The salt possessed the following constants: m. p. 148° (corr.) (1.6° rise per minute) and $(X)_D^{26}$ -76.5° (1 per cent solution in dioxan).

III

A one gram sample of l-abietic acid was dissolved in 50 cc of acetone and the solution heated to 50°C., then five cubic centimeters of 15 N NH_4OH was added to the hot solution (large excess was used). On cooling, the solution formed a jelly-like mass which was dissolved in a hot mixture of 25 cc of acetone and 50 cc of ethyl alcohol. Upon cooling the solution over-night, the salt came out as fine white needles which were filtered and recrystallized from hot alcohol. The recrystallized salt, after being thoroughly dried, possessed the following physical constants: m. p. 153.5° (corr.) (1.3° rise per minute) and $(X)_D^{28}$ -75° (1 per cent solution in dioxan).

EXPERIMENTAL DEHYDROGENATIONS CARRIED OUT IN THE CARIUS FURNACE

The introductory work on dehydrogenation was carried out in the Carius furnace, and several successful dehydrogenations were performed on small samples of l-abietic acid. Isosation of dehydroabietic acid was difficult problem, as the separation of the mixture of "pyro" acids involved a large number of operations. Although procedures for the isolation of dehydroabietic acid were found in the literature (see footnotes 8 and 9, page 7), they had to be modified considerably. The yields obtained, due to the small size of sample taken, were probably much lower than would be expected if a sufficiently large sample could have been taken to make mechanical losses insignificant. Hydrogen acceptors were used; however, the work did not progress far enough to indicate the effectiveness of the acceptor.

I

A 60 cm Carius tube was charged with the following substances:

1. Three grams of l-abietic acid; m. p. 164-167° (corr.) (1.5° rise per minute) and $(X)_D^{25}$ -80°.
2. Thirty cubic centimeters of 95 per cent EtOH.
3. Two cubic centimeters of thiophene free benzene (hydrogen acceptor).

4. One gram of asbestos supported palladium (17).

The Carius tube was sealed and placed in a large four tube furnace. As the tube could not be placed in the furnace after equilibrium heating conditions had been reached, a temperature range was maintained between 175 and 215°C., for five hours and twenty minutes. After allowing the tube and furnace to cool over-night, the tube was opened and the contents washed out with 150 cc of 95 per cent EtOH through a buchner funnel in order to remove the suspended catalyst. The volatile constituents were distilled from the filtrate (b. p. range 78-81°) leaving a light yellow residue which solidified on cooling, this residue was dissolved in 150 cc of ether and the ether solution extracted with two successive 100 cc portions of 1 per cent NaOH and finally with one 50 cc portion of base. The aqueous layer was light yellow and the ether layer colorless, indicating only traces of neutral components. The alkaline solution was acidified by the addition of 300 cc of 0.25 N HCl, whereupon the "pyro" acid precipitated as a light tan material. This compound was crystallized from aqueous alcohol with considerable difficulty; however, two grams of semi-crystalline acid was obtained.

Sulfonation of the "pyro" acid was accomplished by adding it to 25 cc of sulfuric acid (sp. gr. 1.835) at -5°C. over a period of thirteen minutes. The solution was stirred

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[17]Littmann, J. Am. Chem. Soc., 60, 1420 (1938).

mechanically for an additional thirty minutes after all of the acid had been added, and the heavy red liquid which resulted was poured into a mixture of 500 cc of ice and water. After the dirty white sulfonation product was filtered, it was washed with water until the washings clouded the filtrate. Hot water was passed through the buchner funnel containing the sulfonation product, whereby the water soluble sulfodehydroabietic acid passed into the receiver. Dihydroabietic acid and tetrahydroabietic acid as the lactones remained on the filter in the form of a light yellow gum. The filtrates were boiled down until the sulfodehydroabietic acid began to crystallize. In the case of the aqueous filtrate obtained by hot water extraction, it was necessary to add a few cc of concentrated sulfuric acid (sp. gr. 1.835) in order to obtain crystallization.

After the sulfodehydroabietic acid was filtered and washed with water, it was placed in a round-bottomed flask containing 75 cc of concentrated sulfuric acid in 100 cc of water. The mixture was brought to the reflux temperature and refluxed for ten hours, during which time the appearance of the suspended acid changed from fine white needles to small clumps of white material. An equal volume of water was added to the hydrolysis mixture and the flask and contents set aside to cool. After the hydrolysis mixture was filtered, the solid material was treated with hot water, and it was found

that a considerable portion of the solid consisted of unchanged sulfodehydroabietic acid. This acid was recovered and the hydrolysis continued in a mixture of 50 cc of sulfuric acid and 50 cc of water. Hydrolysis appeared to be complete after 35 minutes of refluxing. The hydrolysis mixture was treated as previously described and it was found that the hydrolysis had been complete, in as much as no water soluble residue remained. The two fractions of crude dehydroabietic acid obtained were crystallized from aqueous alcohol after being clarified with "Nuchar XXX" in a hot alcoholic solution. After drying the crystalline dehydroabietic acid in the Abderhalden apparatus over phosphoric anhydride, the acid was found to possess the following physical constants: m. p. 172-173.5° (corr.) (1.25° rise per minute) and $(X)_D^{30}$ plus 60° (1 per cent solution in 95 per cent EtOH). The most recent constants found in the literature for dehydroabietic acid are:m. p. 173, 172-173, and 173-173.5; and $(X)_D$ plus 60 to 62°.

A yield of 0.8 gram of dehydroabietic acid was obtained from 2.0 grams of "pyro" acid. The loss of one gram of "pyro" was probably due to occlusion in the catalyst as well as mechanical loss in the isolation from the reaction vessel. Calculating the yield of dehydroabietic acid from the quantity of "pyro" acid used, a yield of 40 per cent was realized. When calculated from the weight of l-abietic acid used, the yield was 26 per cent.

II

A Carius tube was charged with the following substances:

1. Five grams of l-abietic acid.
2. One and five tenth grams of asbestos supported palladium catalyst.
3. Five cubic centimeters of thiophene free benzene.
4. Twenty-five cubic centimeters of EtOH.

The tube was sealed and placed in the furnace where it was heated for five and a half hours. During this heating period the temperature was held between 215 and 230° with the exception of one hour when it rose to a maximum of 255°. After allowing the furnace and tube to cool over-night, the tube was opened and the contents washed through a buchner funnel with EtOH. The alcoholic filtrate was heated to 75° and water added to incipient turbidity. On cooling, the "pyro" acid came down as a white semi-crystalline solid. This acid was filtered and the filtrate boiled down to dryness. Then the small amount of residue remaining was extracted with 1 per cent of NaOH from an ether solution, and the aqueous layer acidified with dilute HCl, whereupon the remainder of the "pyro" acid precipitated. A total yield of 4.5 grams of the acid was obtained.

The "pyro" acid was sulfonated at 0°C., by adding it to 30 cubic centimeters of conc. sulfuric acid. The mixture was stirred mechanically during the addition and for an

additional 30 minutes after all the acid had been added. The reaction product was poured into a mechanically stirred mixture of 1.5 liters of ice and water, and the precipitated sulfonation product filtered. After extracting the sulfodehydroabietic acid with hot water, the filtrates were boiled down to a small volume. The original filtrate containing excess sulfuric acid precipitated the sulfodehydroabietic acid, whereas the filtrate obtained from the hot water extraction formed a jell on cooling. The gelatinous mixture was warmed and several cc of concentrated sulfuric acid added. After the solution was cooled, the sulfonic acid precipitated. The sulfonation product was clarified with activated charcoal (Nuchar XXX" and then hydrolyzed by refluxing in a mixture consisting of 100 cc of water and 100 cc of concentrated sulfuric acid (sp. gr. 1.835) (60 per cent sulfuric acid) for 1.5 hours. As was found in the previously described experiment, hydrolysis had been incomplete and the unchanged sulfodehydroabietic acid was recovered and hydrolysis continued in 150 cc of 60 per cent sulfuric acid for forty-five minutes. Both samples of crude dehydroabietic acid obtained were dissolved in hot ethyl alcohol and the solutions clarified with activated charcoal. After filtering the mixture, the filtrate was heated and brought to incipient turbidity by the addition of water. Two grams of crystalline dehydroabietic acid was obtained, calculated on the amount of "pyro" acid used the yield was 44 per cent. On the basis of the original 5 grams of l-abietic acid used,

the yield was 40 per cent. The dehydroabietic acid obtained possessed the following physical constants: m. p. 171-172.5° (corr.) (1.1° rise per minute) and $(X)_D^{25}$ plus 62°.

III

Charge for the Carius tube:

1. Seven grams of Commercial Abietic Acid containing 87 per cent acids.
2. One gram of asbestos supported palladium catalyst.
3. Twenty-five cubic centimeters of 95 per cent EtOH.
4. Five cubic centimeters of thiophene free benzene.

The sealed tube was placed in the furnace and a temperature of 175-200° maintained for three hours. After allowing the furnace to cool over-night, the tube was opened and the contents washed through a buchner funnel with the aid of alcohol. An attempt was made to bring the "pyro" acid to incipient crystallization by the addition of water to a hot alcoholic solution of the acid; however, a semi-solid gum was obtained. This material was dried under vacuum and finally crushed so that a sulfonation could be carried out. The "pyro" acid was added to 30 cc of mechanically stirred concentrated sulfuric acid at 0 to 5°C. After the acid had been added, stirring was continued for an additional thirty

minutes. The mixture became homogeneous after standing overnight in the refrigerator. The dark reddish-brown solution was poured slowly into 800 cc of ice and water, whereupon the sulfonation product precipitated as a light tan flocculent material.

The sulfonation product was filtered, washed with water, and the filtrate boiled down until the sulfonic acid began to precipitate. The sulfonation mixture on the buchner funnel was treated with hot water until an intractable yellow gum remained. The filtrate was made strongly acid with concentrated HCl and allowed to cool, whereupon the sulfonic acid precipitated. Both batches of sulfodehydroabietic acid were filtered, combined, redissolved in hot water, and the solutions clarified with activated charcoal. The sulfodehydroabietic acid was precipitated by the addition of a few cc of concentrated sulfuric acid. This acid was filtered, and after drying, 3.6 grams or an approximate yield of 46 per cent was obtained.

DESCRIPTION OF HIGH PRESSURE DEHYDROGENATION APPARATUS

The use of the Carius furnace was limited in two respects, the most important of which was the small size of the charge which had to be used. Another disadvantage was the impossibility of pressure regulation. To overcome both of these difficulties a high pressure bomb was built which could easily take samples of acid up to 40 or 50 grams.

The bomb consisted of two parts: the reaction chamber and the bomb head assembly. The reaction chamber was made from a solid cylinder of high pressure steel (Chrome Vanadium Steel S. A. E. No. 6140) and had an inside volume of 280 cc. The bomb head was of an advanced design and was threaded to turn into the reaction chamber; it was constructed in such a manner that increased internal pressure caused a tighter joint to be made at the gaskets. A three or ten thousand pound guage was attached to the head and a needle valve completed the assembly.

The bomb was set in an electrically heated container and the entire assembly mounted on a mechanical shaking machine. Temperature control was maintained by means of a bi-metal coil set in the base of the bomb and activated by an electronic relay (18). Temperature control under operating conditions was maintained over a 5 to 10° range.

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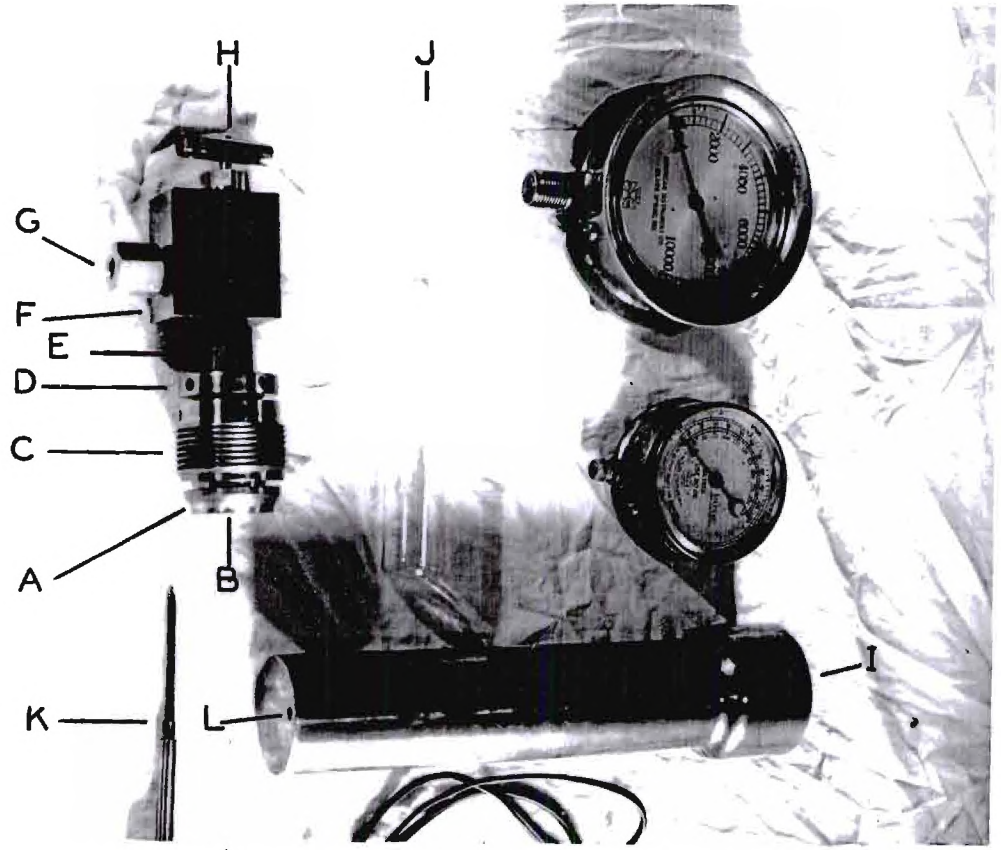
[18]Serfass, Ind. Eng. Chem. Anal. Ed., 13, 262 (1941).

Figure IV

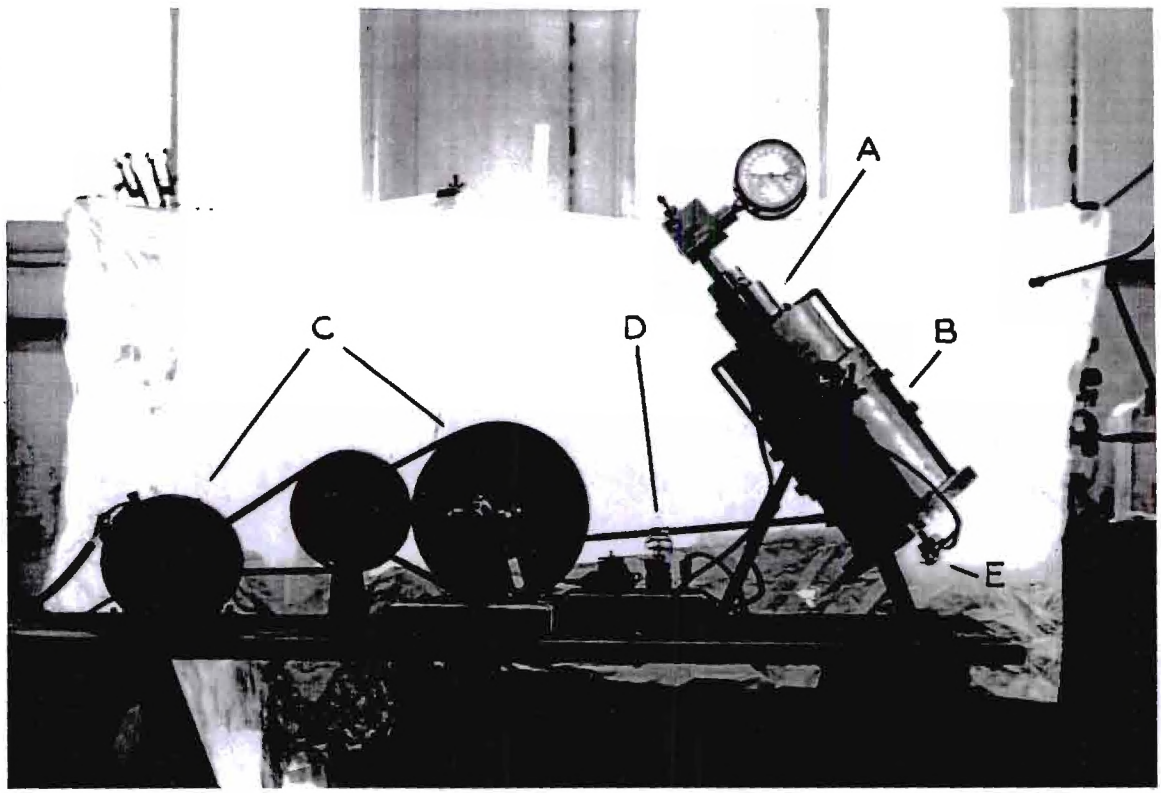
High Pressure Bomb Dismantled



A. Gasket (copper)
B. Plunger
C. Threaded Plug
D. Lock Nut
E. Connecting Threaded Nipple
F. Valve Block
G. Guage Adapter
H. Needle Valve Handle
I. Reaction Chamber
J. Glass Liner
K. Bi-Metal Coil
L. Receptacle for Bi-Metal Coil

Figure V

Complete Dehydrogenation Apparatus



A. High Pressure Bomb

B. Electrically Heated Container

C. Shaking Machine

D. Thermo-Regulator

E. Bi-Metal Coil

EXPERIMENTAL

Three dehydrogenations were attempted using 25 and 30 gram samples of l-abietic acid. An asbestos supported palladium calalyst was used with thiophene free benzene as the hydrogen acceptor. In each of the three cases, leaks developed around the gaskets and very poor yields of sulfodehydroabietic acid were obtained by the procedures outlined in the work with the Carius furnace.

After replacing the bronze gaskets with copper the leaks in the system were stopped. Bronze gaskets appeared to be too hard to form a gas tight fit, although the bomb was tested to 6000 pounds per square inch with a hydraulic press and the bronze gaskets were able to withstand this type of pressure. A glass liner was made for the bomb to facilitate the removal of the reaction mixture. Fittings were made to enable pressure to be built up in the bomb from a tank of nitrogen gas. At this point, work was discontinued on the project for the time being, and in the interest of future work the following observations and suggestions are of considerable value:

1. The reaction should be carried out at a temperature between 225 and 250^{o}C.
2. The initial pressure should be varied so as to maintain the reaction in the liquid phase. The required pressure should be about 300 to 1000

pounds per square inch and will depend upon the quantity of solvent and other liquids present.

3. Although asbestos supported palladium catalyst gave good results the use of raney nickel (19) and alumina (20) supported catalysts should be investigated.

4. To speed up the isolation of a product from the reaction mixture (a derivative of dehydroabietic acid being necessary) the procedure could be stopped at the isolation of sulfodehydroabietic acid and knowing the yield which could be expected in the hydrolysis the yield of dehydroabietic acid could be calculated. A procedure which has been investigated and appears to be somewhat better than the hot water extraction of sulfodehydroabietic acid is described by Fleck and Palkin (21).

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[19]Covert and Adkins, J. Am. Chem. Soc., 54, 4116 (1932).

[20]Adkins, Richards, and Davis, J. Am. Chem. Soc., 63, 1325 (1941).

[21]Fleck and Palkin, J. Am. Chem. Soc., 61, 248 (1939).

SUMMARY

Investigation of the use of the 1/4 sodium salt of l-abietic acid as a means of obtaining the pure acid indicated that the method employed leads to a more rapid isolation of the pure acid that the procedure described in the literature.

The bulk of the work dealt with the use of an ammonium salt of l-abietic acid of indefinite composition, and when this salt was purified by crystallizing three times from a mixed solvent consisting of acetone and dioxan, an acid was obtained possessing the properties of pure l-abietic acid. Two different procedures were devised for the preparation of the crude ammonium salt and several solvents were described which could be used in crystallizing the salt. The half-ammonium salt was prepared (this salt has apparently not been described in the literature as is also true of the crude salt)from the pure acid.

The work on dehydrogenation did not progress far enough to indicate the effectiveness of the catalyst or hydrogen acceptors used. Considerable time was required to master the technique involved in isolating the final products; however, the results obtained in the Carius furnace indicated that under the proper conditions, dehydroabietic acid could be isolated in good yield.

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